The Alkylation of Benzene, Toluene and Naphthalene

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DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

By

THOMAS MORRIS BERRY

Baltimore, June, 1923

Easton, Pa.:
Mack Printing Company
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THE ALKYLATION OF BENZENE, TOLUENE AND NAPHTHALENE

It was shown by Balsohn[1] that ethylene may be substituted for ethyl chloride in the Friedel and Crafts synthesis. Milligan and Reid[2] found that the reaction is facilitated by high-speed stirring to such an extent that this becomes a convenient method for the ethylation of benzene.

The present investigation has to do with a further study of the reaction and with its extension to propylene and cyclohexene.

The ethylene (or propylene) is passed into the benzene at such a rate that only an occasional bubble escapes. If an excess of gas passes through, hydrogen chloride is carried away and the reaction slows down. It is usually possible to restore the original speed by passing in a small amount of dry hydrogen chloride.

In the ethylation of benzene, ethylene is not to be considered as simply a substitute for ethyl chloride. For every molecule of ethyl chloride that reacts, one of hydrogen chloride is eliminated. This escaping as a gas carries off with it much of the volatile ethyl chloride. The utilization of ethyl chloride depends on the rate at which it is passed. At 0.01 mole per minute per mole of benzene only 25% of it reacts, while at one-fourth of this rate 43% reacts. Ethylene may be completely absorbed at these rates.

Drying the benzene with sodium gave decidedly better results than using only calcium chloride. The runs were made at about 70°, though there appears to be little difference in the rate between 60° and 90°. There is usually an incubation period of about twenty minutes before much ethylene is absorbed. Refluxing for several minutes appears to shorten this. The addition of 10% of higher ethylated benzenes from a previous run may hasten the starting of the reaction. The speed increases with the accumulation of ethylated benzenes, reaching a maximum when about 4 equivalents of ethylene have been absorbed, remaining nearly constant for a while and then declining.

The apparatus used was that described by Milligan and Reid,[2b] the stirrer being run at 7000 to 8000 r.p.m.

As is well known, all of the possible ethylation products are formed and no way has been found of directing the process to the production of any one, exclusively. Some hexa-ethylbenzene is present when less than 0.5 mole of ethylene has been absorbed and less than half of the benzene has

[1] Balsohn, *Bull. soc. chim.*, [2], **31**, 539 (1879).

[2] (a) Milligan and Reid, *J. Am. Chem. Soc.*, **44**, 206 (1922); (b) *Ind. Eng. Chem.*, **15**, 1048 (1923).

been attacked. Data from a number of runs are given in the experimental part. As the conditions under which the runs were made were not all the same and as the separations were made by fractionation the figures are not strictly comparable or very exact but these conclusions may be drawn. As the reaction progresses, mono-ethylbenzene increases regularly to about 30% when about 1.1 mole of ethylene has been passed in. Diethyl- and tetra-ethylbenzene never go much above 20%. The penta-ethyl is present almost from the first but its concentration is remarkably low and nearly constant to the end. There seems to be a preferential formation of the triethyl which constitutes over 50% of the mixture when somewhat over 3 moles of ethylene have reacted. In subsequent work as high as 80% of triethyl has been found. Hexa-ethyl benzene appears early and always exceeds the tetra- or penta-. It steadily increases until it constitutes nearly 90% of the mixture, when the mixture becomes too nearly solid to stir. There is no difficulty in preparing hexa-ethylbenzene in one operation, but on account of the large increase in volume it is usually more convenient to stop the reaction when three equivalents of ethylene have been introduced, separate and use this material for a new run.

The best proportion of aluminum chloride seems to be 1 mole ($AlCl_3$) to about 13 of benzene. When the stirring is stopped the reaction mixture separates sharply into two layers. The top one is clear and colorless and contains only a trace of aluminum chloride. The lower layer is dark and viscous and consists of aluminum chloride associated with something like its own weight of hydrocarbons. In a few runs this lower layer has been worked up separately. As the amount of this layer is relatively small the results on it are not as exact as could be desired but they do show that each of the hydrocarbons present is partitioned between the two layers and that the aluminum chloride holds the higher ethylated benzenes in preference to the lower. From mono- to tetra-ethylbenzene the concentrations in the two layers do not differ greatly but there is a marked heaping up of penta-ethylbenzene in the lower layer which always contains more of it than of either the tetra- or hexa-. The hydrocarbon which is most abundant in the lower layer always contains one or two more ethyl groups than the one that predominates in the upper. Toluene is more readily ethylated than benzene, and bromobenzene less so. Both give complicated mixtures which contain the expected products.

Gustavson[3] prepared *iso*propylbenzene from propyl bromide and benzene in the presence of aluminum chloride with 34% yield. Propylene does not seem to have been used for this purpose. Propylene is taken up by benzene under the same conditions as ethylene but only about 4% as rapidly. The product separates into two layers, the lower being relatively larger and slower to react with water than in the ethylation

[3] Gustavson, *Ber.*, **11**, 1251 (1878).

of benzene. It was impracticable to carry the fractionation above 290° as the residue above this was a tarry mass. Hence the propylated benzenes were separated only as far as the tetra-. From some of the higher fractions a well crystallized solid separates, m. p. 117° and b. p. 260° at 775 mm. This appears to be 1,2,4,5-tetra-*iso*propylbenzene. Of the di-*iso*propylbenzenes the meta seems to predominate, as does the symmetrical among the tri-.

As in ethylation the rate increases as propylation progresses. With mono-*iso*propylbenzene it is double and with the tri- it is 10 times what it is with benzene.

A curious phenomenon is the formation of two aliphatic hydrocarbons, b. p. 28°; d_6 0.7095 and the other b. p. 56–59°. The latter is probably di-*iso*propyl.

Toluene is more readily propylated than benzene, the chief product seeming to be *p*-cymene. Naphthalene was propylated by the transfer of *iso*propyl groups from di-*iso*propylbenzene.

Cyclohexane reacts with benzene when aluminum chloride is added to a mixture of the two. Some cyclohexylbenzene is obtained but the most of the product is high boiling. The results are similar to those obtained by Kursanoff,[4] who used cyclohexyl chloride.

Experimental

The details of the runs with ethylene are given in the table below. The regular amount of benzene was 300 g., 3.85 moles, but 455 g., 5.83 moles, was used in Runs 4 and 5. In Run 10, 363 g., 2.24 moles, of triethylbenzene was used instead of benzene as starting material and similarly 300 g., 2.24 moles, of diethylbenzene in Run 11. The ethyl groups in these were counted in calculating the ratio of ethylene to benzene. The rate of stirring was 7200 to 8200 r.p.m. The ethylene put in is in moles per mole of benzene. The largest amount of ethylene put in during a run was 352 l. in 675 minutes in Run 9. The highest rate was in Run 11, 402 cc. per minute per mole. At the end of a run the product was drowned, the oil layer washed, dried and fractionated through a Vigreux column. The results are given in the following tables.

In four of these runs the two layers were separated and worked up separately. The compositions of the upper and lower layers and their ratios are given in Table II.

On account of the smallness of the amounts of the hydrocarbons in the lower layers, the figures for the lower layers are not as accurate as for the upper. Run 8 showed a high percentage of the penta- in both layers. The highest in each layer is starred. The relative weights of the hydrocarbons in the two layers were 16, 12, 12 and 13 to 1.

[4] Kursanoff, *Ann.*, **318**, 310 (1901).

TABLE I

COMPOSITION OF PRODUCT IN MOLES PER 100 MOLES OF BENZENE

Run	Moles of ethylene	Benzene	Mono-	Di-	Tri	Tetra-	Penta-	Hexa-
1	0.20	87.9	10.9	1.24	...	...	..	..
2	0.50	80.8	15.5	2.14	0.67	0.15	0.06	0.67
3	0.56	80.5	15.2	1.67	0.71	...	..	1.91
4	1.14	31.6	35.2	21.1	4.0	2.4	2.8	2.82
5	1.19	31.0	36.9	22.7	5.1	1.8	1.2	1.16
6	1.27	49.6	26.7	11.2	3.9	1.2	0.60	6.7
7	1.38	37.3	30.1	11.6	6.7	3.00	3.2	8.2
8	1.68	35.4	23.4	13.6	6.3	4.2	3.6	13.4
9	3.66	0.2	1.1	10.6	56.2	11.6	1.5	18.7
10	5.24	..	..	..	7.00	18.8	2.4	71.8
11	5.74	..	..	..	...	8.5	0.9	90.6

TABLE II

COMPOSITIONS OF THE TWO LAYERS IN MOLAR PER CENT.

Run	Ethylene	Layer	Benzene	Mono-	Di-	Tri-	Tetra-	Penta-	Hexa-
5	1.19	Upper	32.3	37.7*	21.7	4.6	1.8	0.9	1.0
		Lower	5.0	22.3	43.3*	15.5	3.8	6.7	3.4
		Ratio	0.16	0.6	2.0	3.4	2.1	7.1	3.4
7	1.38	Upper	39.7*	28.8	10.9	6.7	2.8	1.8	9.2
		Lower	..	45.8*	20.8	2.8	4.6	22.2	3.7
		Ratio	..	1.6	1.9	0.4	1.6	12.2	0.4
8	1.68	Upper	35.4*	22.6	13.6	6.0	4.0	5.0	13.4
		Lower	17.6	22.0*	6.6	7.7	4.9	35.2*	6.0
		Ratio	0.5	1.0	0.5	1.3	1.2	7.0	0.5
9	3.66	Upper	.2	1.1	10.6	55.5*	12.0	1.3	19.3
		Lower	..	..	4.6	33.8	19.0	42.2*	0.4
		Ratio	..	..	0.4	0.6	1.6	33	.02

The Ethylation of Toluene.—Ethylene was passed into 280 g., 3.04 moles, of toluene under the usual conditions. Absorption was at the rate of 266 cc. per minute per mole of toluene and 0.9 equivalent was taken up in 81 minutes. Distillation of the product gave the following.

TABLE III

PRODUCTS FROM THE ETHYLATION OF TOLUENE

Boiling range, °C.	Weight, g.	Probable constituents
Up to 120	45	Toluene
120–145	42	Ethylbenzene and xylenes
145–164	121	Ethyltoluenes
164–207	93	Higher substitution products
Above 207	5	Higher substitution products

The part boiling from 198–203° was strongly fluorescent.

The Ethylation of Bromobenzene.—Into 484 g., 2.83 moles, of bromobenzene containing 0.37 mole of aluminum chloride one equivalent of ethylene was passed. It was taken up at the rate of 70 cc. per mole per minute.

Distillation of the product gave the following.

TABLE IV

PRODUCTS FROM THE ETHYLATION OF BROMOBENZENE

Boiling range, °C.	Weight, g.	Probable constituents
Up to 140	15	Benzene and ethylbenzene
140–180	135	Ethyl- diethylbenzenes
180–215	86	Brominated ethylbenzenes
215–250	115	Brominated ethylbenzenes
Above 250	85	Tarry residue

At 240–250° decomposition began with evolution of hydrobromic acid.

The Propylation of Benzene.—Propylene was made by dropping *iso*propyl alcohol[5] on to metaphosphoric acid heated to 500° or above. This method gives an excellent yield of pure propylene but is troublesome on account of the destructive action of the phosphoric acid on the Pyrex flask. Propylene was also prepared by passing the *iso*propyl alcohol vapor over pumice impregnated with alumina and kept at 600°. The propylene was collected over water and purified as was the ethylene.

The runs with propylene were in every way similar to those with ethylene but were less numerous. Two runs were made starting with benzene, two with mono-*iso*propylbenzene and one with tri-*iso*propylbenzene. The distillations of the products were stopped at about 280°, as above that temperature decomposition seemed to set in. The penta- and hexa-*iso*propylbenzenes, if they were formed, were left in the residue.

The reaction product separates into two layers as in the ethylation of benzene, but with propylene the lower layer is relatively larger and the aluminum chloride complexes which it contains are decomposed by water more slowly than are those obtained in the ethylation of benzene. Usually only about three-fourths of the hydrocarbons contained in it boil below 285°.

For four runs the compositions of the product in percentages by weights were:

TABLE V

PRODUCTS FROM THE PROPYLATION OF BENZENE, PERCENTAGE BY WEIGHT

No.	Moles of propylene	Benzene	Mono-	Di-	Tri-	Tetra-	Residue
1	0.6	16.3	42.5	27.0	6.1	2.1	6.1
2	0.75	18.9	52.0	20.0	3.0	1.3	4.8
3	1.97	1.4	0.6	3.9	87.6	3.3	3.3
4	1.93	1.3	15.6	46.7	31.0	5.4	...

In three of these runs the two layers were worked up separately with the following results.

[5] Our thanks are due to the Standard Oil Co. of N. J. for a generous supply of *iso*propyl alcohol.

TABLE VI

COMPOSITIONS OF THE TWO LAYERS IN PERCENTAGES BY WEIGHT AND THEIR RATIOS

Run	Propylene	Layer	Benzene	Mono-	Di-	Tri-	Tetra-	Residue
1	0.6	Upper	15.7	45.9	30.8	5.2	1.2	1.2
		Lower	18.8	28.6	11.1	9.7	5.6	26.1
		Ratio	1.2	0.62	0.36	1.9	4.7	22
2	0.75	Upper	19.2	55.0	22.4	2.2	..	1.2
		Lower	17.4	32.6	9.9	6.6	1.6	25.3
		Ratio	0.9	0.59	0.44	3.0	..	21
3	1.97	Upper	1.5	0.5	4.2	88.7	3.0	2.1
		Lower	..	1.1	1.1	71.7	15.2	10.9
		Ratio	..	2.2	0.25	0.9	5.1	5.2

In these runs the relative weights of the hydrocarbons in the upper and lower layers were 3.5, 4.5 and 10.3 to 1.

The product from Run 4 was fractionated repeatedly. The final results were as follows.

The indications are that about 65% of the di-*iso*propyl is the meta and that the 1,3,5-tri-*iso*propyl is about 75% of that group.

It was found particularly easy to propylate the tri-*iso*propylbenzene fraction; 250 g. of it took up 56 liters of propylene in twelve hours. On cooling,

TABLE VII

FRACTIONATION OF THE PRODUCT FROM RUN 4

Temp. range, °C.	Weight, g.	Probable constituents
Up to 75	17	Aliphatic hydrocarbons
75 - 90	20	Benzene
152 -156	220	*Iso*propylbenzene
150 -201	25	Mono- and di-
201 -203.5	33	*m*-Di-*iso*propylbenzene
203.5-204.5	410	*m*-Di-*iso*propylbenzene
204.5-208.5	68	Mixture
208.5-209.5	119	Di-*iso*propylbenzene (?)
209.5-233	84	Mixture of di- and tri-
233.5-234.5	256	1,3,5-Tri-*iso*propylbenzene
234.5-246	164	Tri-*iso*propylbenzenes
Above 246	61	Tetra- and higher

the product solidified, and by centrifuging white crystals were obtained. After several recrystallizations from alcohol this material melted at 117° and boiled at 260° under 775 mm. Some of it was oxidized by long heating with potassium permanganate solution and an acid obtained which melted at 282°. Mellitic acid melts at 286° and the di-anhydride of 1,2,4,5-benzenetetracarboxylic acid melts at the same temperature. The hydrocarbon is probably the 1,2,4,5-tetra-*iso*propylbenzene as its boiling point, 260°, seems much too low for the hexa-*iso*propyl. Hexa-ethylbenzene boils at 294° and the hexa-*iso*propyl should boil at least that high. The 1,2,4,5-tetramethylbenzene is a solid and boils below its isomers.

TABLE VIII

ANALYSIS OF THE HYDROCARBON

	Found, %		Calculated for Tetra-	Penta-	Hexa-
Carbon	87.43	87.60	87.72	87.41	87.18
Hydrogen	12.43	12.61	12.28	12.59	12.82

Assuming that the carbon found is low and the hydrogen high the analysis indicates the tetra-.

By repeated fractionation a quantity of 1,2,4-tri-*iso*propylbenzene was separated. It boils at 237–237.5° at 752 mm., 97–97.5° at 4 mm.; d_0^0 0.8764 and d_{25}^{25} 0.8593, N_D 1.4855 at 25°. It was identified by oxidation to an acid which melted, with formation of the anhydride, at 214°, which corresponds to the 1,2,4-benzenetricarboxylic acid.

The oils boiling below 75° were refractionated and separated into two hydrocarbons, one boiling at 28°, d_0^0 0.7095 and the other boiling at 56–59°. The latter is evidently di-*iso*propyl, which boils at 58°.

The Propylation of Toluene.—Toluene reacted somewhat faster than did benzene under the same circumstances. From 662 g. of toluene which had taken up 0.3 equivalent of propylene the following fractions were obtained.

TABLE IX

PROPYLATION OF TOLUENE

Boiling range, °C.	Weight, g.	Probable constituents
Up to 105	5	Benzene
105–120	370	Toluene
120–145	17	Xylenes
145–170	25	Tri-ethylbenzene and cymenes
170–185	161	*m*- and *p*-Cymenes
Above 185	60	

As the cymenes boil too close together for fractionation, advantage was taken of the fact that their bromine derivatives boil 10° apart, that of the meta at 224° and that of the para at 234°. A portion of the 170–185° fraction was brominated and 80% of the product was found to boil between 228° and 240°, indicating a preponderance of the *p*-cymene.

The Propylation of Naphthalene.—Naphthalene was stirred with di-*iso*propylbenzene in the presence of aluminum chloride. From 217 g. of naphthalene and 132 g. of di-*iso*propylbenzene at 90° for 4.5 hours, 15 g. of a fraction boiling at 264–266° was obtained. This was probably *iso*propylnaphthalene. One third of the naphthalene was recovered unchanged and there were higher-boiling products which were not identified.

Cyclohexene and Benzene.—As cyclohexene resembles ethylene in many respects, it was thought that it should react with benzene under the usual conditions to give cyclohexylbenzene. To a mixture of 276 g. of benzene and 290 g. of cyclohexene, 60 g. of aluminum chloride was added.

Even without stirring a violent reaction took place. Stirring for thirty seconds would bring the mixture to a boil. After a time the mixture could be stirred continuously. This was done for five hours, during which time the temperature remained at about 55°. The mixture was worked up as usual and gave 50 g. of cyclohexylbenzene, boiling from 230–245°, besides large amounts of high-boiling products. Kursanoff[4] got similar results using cyclohexyl chloride.

Summary

The ethylation of benzene by ethylene in the presence of aluminum chloride with high-speed stirring has been studied. The ethylbenzenes from mono- to hexa- are readily obtained, their relative amounts depending on the proportion of ethylene taken up. Similar results were obtained using propylene. Cyclohexene also reacts with benzene under the same conditions. Toluene and naphthalene may be substituted for the benzene.

BIOGRAPHY

The author of this dissertation was born in Charles Co., Maryland, February 8, 1897. He received his early education in the public schools of Baltimore and graduated from the Johns Hopkins University in 1920 with the degree of Bachelor of Science. In the Fall of 1920 he entered the Johns Hopkins Graduate School of Chemistry, taking as his subordinate subjects, Physical Chemistry and Mathematics. In June, 1922, he received the degree of Master of Arts, the title of his thesis being "The Friedel and Crafts Reaction."

During the years 1921–22 and 1922–23 he was part time instructor in Organic Chemistry at the Mt. Vernon College of Baltimore and the University of Maryland, respectively.

He was appointed a Hopkins Scholar for the years 1920–21, 1921–22 and 1922–23.